Influence of Solutocapillary Convection on Macrovoid Defect Formation in Polymeric Membranes

Alan R. Greenberg, Principal Investigator Departments of Mechanical Engineering University of Colorado at Boulder Boulder, CO 80309-0424

Co-Investigators:

Matthew R. Pekny, Sanjay Konagurthu, Paul Todd, and William B. Krantz Departments of Chemical Engineering University of Colorado Boulder, CO 80309-0424

The appearance of macrovoids (MV's) during the formation of asymmetric polymeric membranes by the solvent-casting process first developed by Loeb and Sourirajan is a common, well-documented occurrence. MV's are generally considered undesirable, as they adversely affect the permeability properties and performance of polymeric membranes for microfiltration, ultrafiltration, and reverse osmosis. However, MV's can be useful in certain thin-film applications in which vapor transmission is necessary, or for use as reservoirs for enzymes or liquid membrane material. Thus, developing processes that can accurately control or prevent MV formation is important to the rapidly growing membrane industry. However, in order to do this, it is highly desirable to first develop a completely predictive model of macrovoid formation.

Currently, two hypotheses concerning the mechanism of MV growth exist. Unfortunately, no experimental studies have yet been able to discriminate between the two. Reuvers^[2] has proposed a nucleation and growth mechanism in which MV growth is driven by pure molecular diffusion of nonsolvent from the surrounding casting solution. Since only diffusion and no force balance is implicit, MV growth should not be influenced by any body forces such as gravity if this hypothesis is correct. Though body forces may influence the initial demixing process of this hypothesis (the nucleation phase, which is common to both hypotheses), it is reasonable to assume that the motion due to these forces will be negligible because of the insignificant mass of the nuclei.

Shojaie^[3] and Shojaie *et al.*^[4] contend that Reuvers' hypothesis is questionable because diffusion alone cannot facilitate MV growth on time scales that can be as short as 2-5 seconds. Thus, they offer an alternate hypothesis based on their work with the cellulose acetate/acetone/water casting system. They claim that evaporation of acetone from the liquid/gas interface during the drycasting process induces a water concentration gradient, which in turn creates a surface-tension gradient that pulls the growing MV downward into the bulk casting solution. There, MV growth is facilitated by convective-diffusion due to bulk flow induced by interfacial (solutal Marangoni) convection, and opposed by both viscous drag and buoyancy forces since the surrounding casting solution is more dense than the growing macrovoid.

Since neither surface tension nor gravity is important in the first hypothesis, varying these parameters should allow one to distinguish which (if either) of these two hypotheses is correct. Thus, four objectives are being pursued in this research:

(1) The number and volume of macrovoids formed in dry-cast cellulose acetate/acetone/ water membranes under varied levels of inertial acceleration are being measured using low-gravity experiments on the NASA KC-135A aircraft, and high-gravity experiments on a geotechnical centrifuge. The structure of the resulting membranes are then analyzed

using scanning electron microscopy. If the hypothesis advanced by Shojaie *et al.*^[4] is correct, it is expected that a wider range of casting solution compositions should give rise to MV-containing membranes when cast in microgravity, and MV's formed in low-g should be larger and more numerous than MV's in membranes cast from solutions of identical composition in 1-g. Opposite effects are expected for membranes cast in increased inertial acceleration. In preliminary experiments, membranes cast by Konagurthu^[1] under low- and high-gravity conditions confirmed these expectations. Additional experimentation is necessary.

- (2) The role of surface-tension-gradient-driven forces is tested by adding surfactant solutes to the casting solution, with careful attention to effects on the phase diagram. Surfactants that reduce the interfacial tension gradient between the growing MV and the surrounding casting solution have been identified, and were shown to decrease the number and size of MV's, suggesting the solutocapillary hypothesis is correct. If Reuvers' hypothesis was correct, the addition of surfactants should not have had a significant impact on macrovoid formation.
- (3) Real-time video microscopy of simulated dry casting reveals the simultaneous motion of the phase inversion front and the migrating, growing macrovoids using casting solutions of various compositions including surfactants. Again, in preliminary experiments the MV growth patterns suggest a convective rather than a diffusive process.
- (4) A complete model of MV growth due to solutocapillary flow that combines experimental measurements with Marangoni convection theory is under development. This model is being coupled with an existing theory for the solvent-casting membrane formation process developed by Shojaie^[3] to yield a completely predictive model for polymeric membrane formation via the dry-cast process. Although this model is being developed using data for the CA/acetone/water system only, it will be readily applicable to other membrane systems as well.

References

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